

# Recent Advances in Hard X-ray Inelastic Scattering with Medium Resolution (A Story about Water)

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*SSRL, Stanford Linear Accelerator Center*

- motivation
- x-ray Raman spectroscopy (XRS)
- x-ray emission spectroscopy (XES)
- selective x-ray absorption (S-XAS)
- resonant inelastic x-ray scattering (RIXS)

# Collaborators



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*Grenoble*

Pieter Glatzel

*Utrecht*

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*LBNL/Davis*

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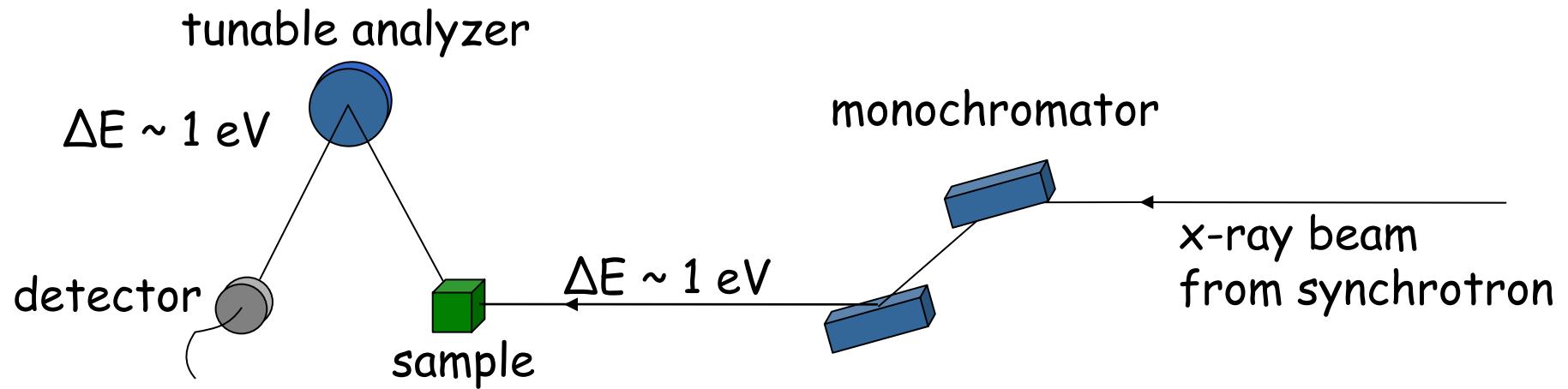
*Calvin Lab, LBNL*

Junko Yano

Beamline Staff

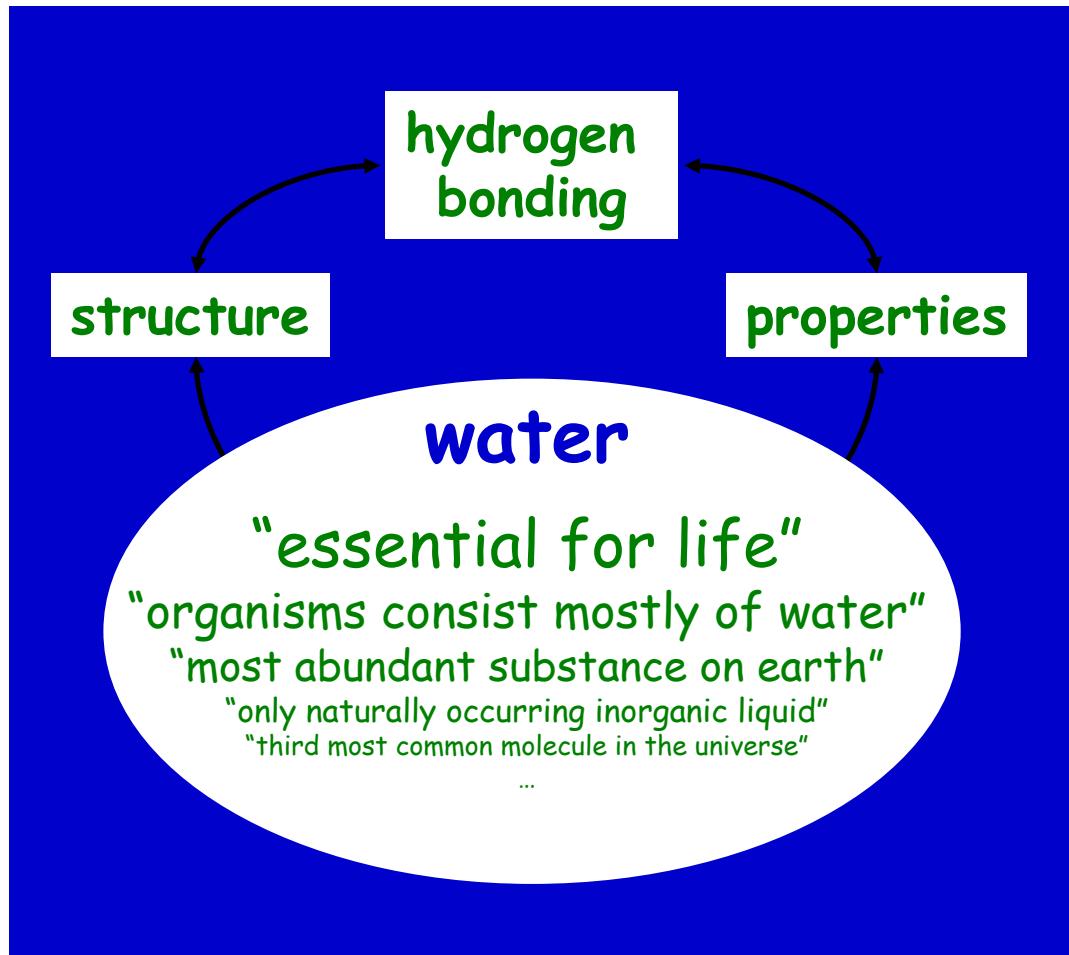
*SSRL 10-2, NSLS X-25, APS 18ID (BioCAT)*

# Photon-in Photon-out X-ray Spectroscopy



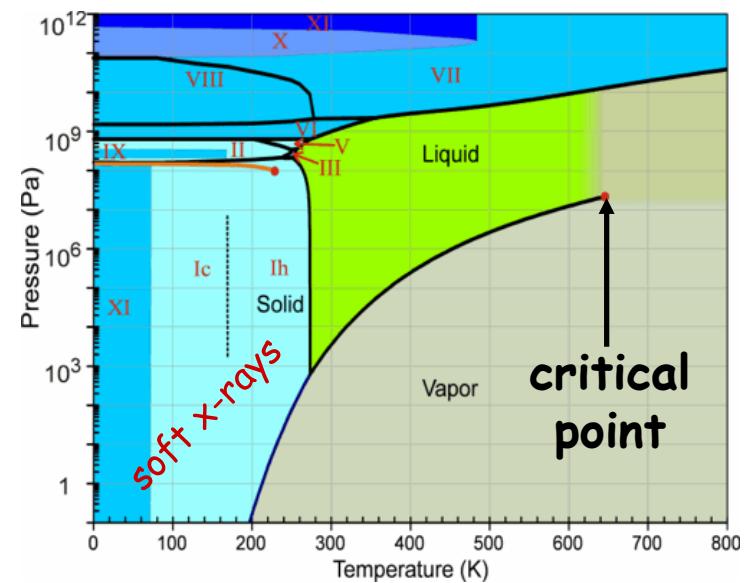
technique	experimental procedure
x-ray Raman scattering (non resonant) selective x-ray absorption	scan of monochromator, analyzer fixed
x-ray emission (non resonant)	scan of analyzer, monochromator fixed
resonant inelastic x-ray scattering	scan of both

# The Local Structure of Water



## experimental techniques:

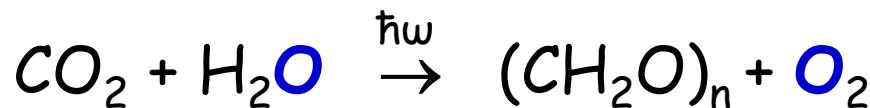
- neutron and x-ray diffraction
  - infrared/fs spectroscopy
  - collective excitations (dynamics)
- **XAS → local structure**





# Photosynthetic Oxygen Evolution

## photosynthesis



this process generates carbohydrates and the world supply of oxygen

### catalytic center

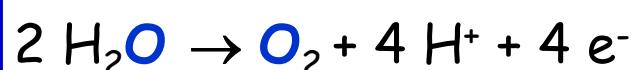
- OEC is a 4 Mn cluster
- four states  $S_0 - S_3$
- EPR, K-edge, EXAFS, K $\beta$ , crystallography
- L-edge not possible

### photosystem II

how? ↓

life cycle

### oxygen evolution



the oxygen is derived from water

### cytochrome oxidase

↓

### aerobic metabolism



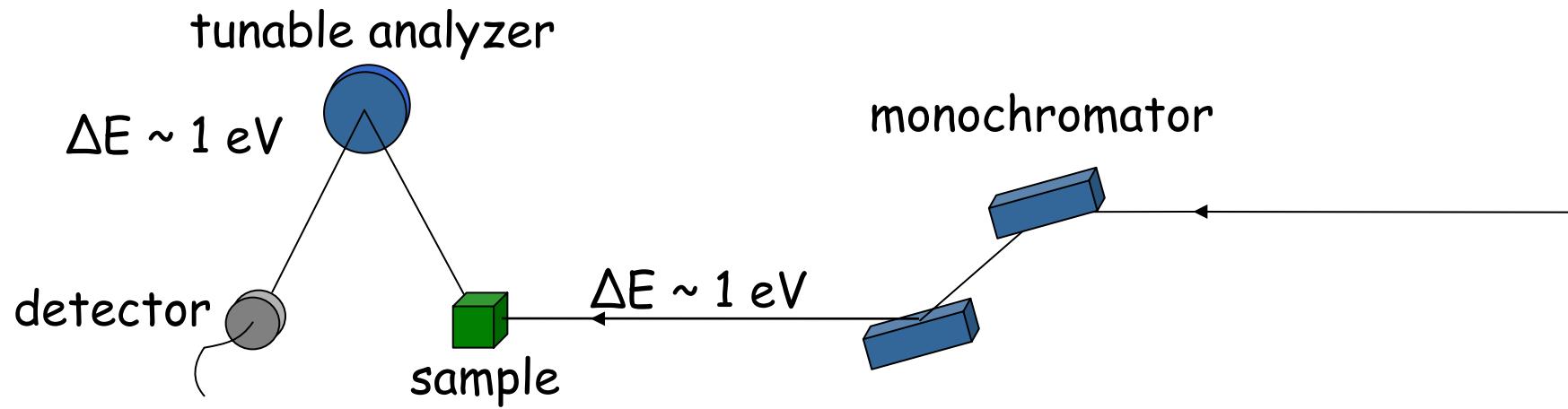
we consume oxygen to "burn" the energy of carbohydrates to produce ATP, the biological energy currency

# Why water?



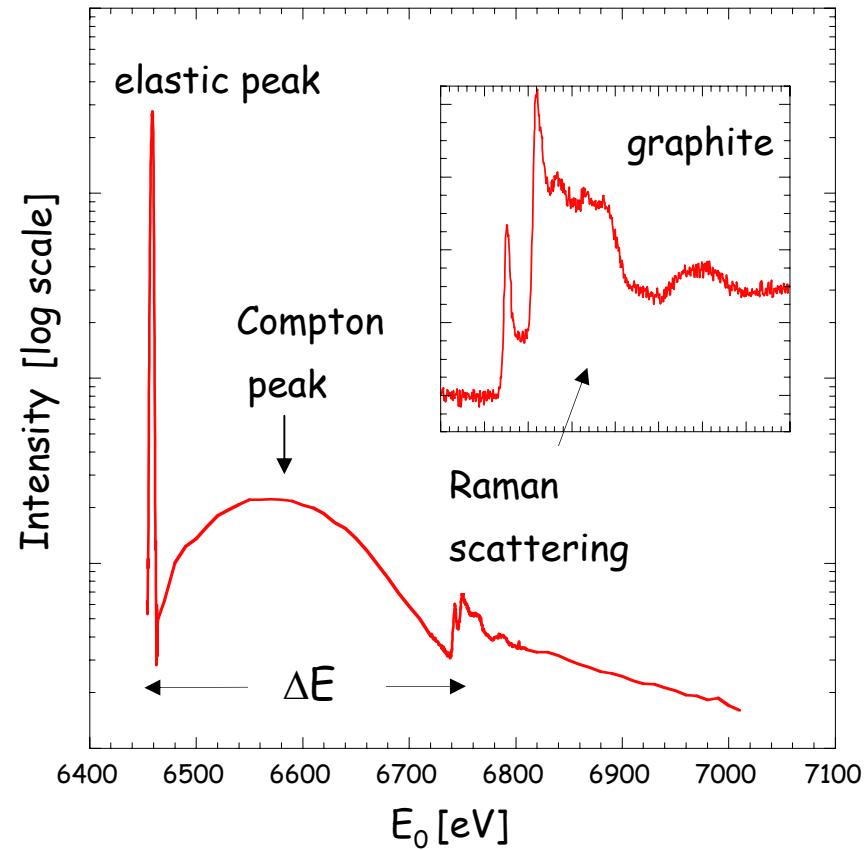
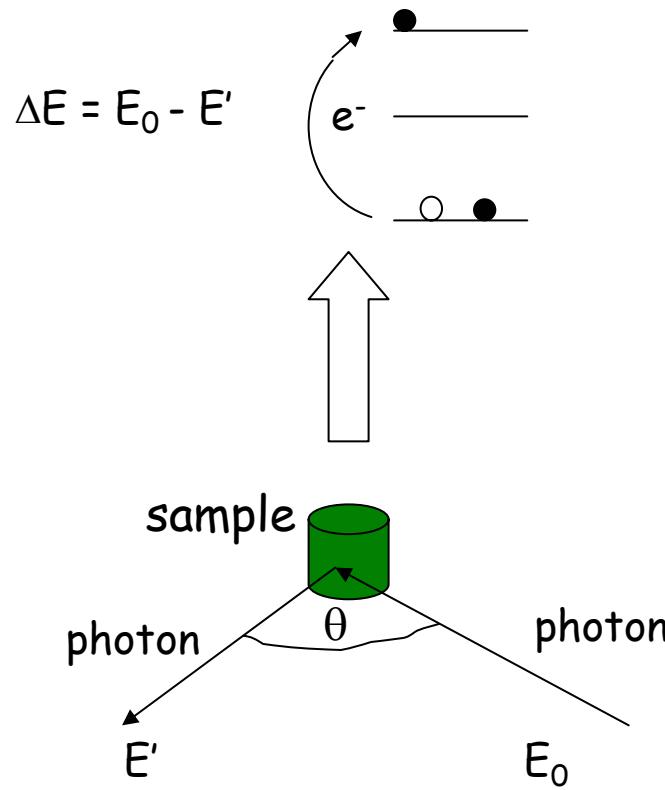
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# Photon-in Photon-out X-ray Spectroscopy



technique	experimental procedure
<u>x-ray Raman scattering (non resonant)</u>	<u>scan of monochromator, analyzer fixed</u>
selective x-ray absorption	
x-ray emission (non resonant)	scan of analyzer, monochromator fixed
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# Principle of X-ray Raman Spectroscopy



scattering probability:  $w \sim \cos^2\theta \sin^2(\theta/2) |\langle i | r | f \rangle|^2$

for  $qr \ll 1$ , and  $|k_i| \approx |k_f|$

# Motivation

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## why XRS?

### sample specific:

- true bulk probe
- no vacuum requirements
- *in situ* experiments
- high temperature/pressure

### technique specific:

- no saturation effects
- non dipole transitions at large  $q$
- pump probe experiments (LCLS)

## samples

### in general:

- any sample with sufficient scattering strength

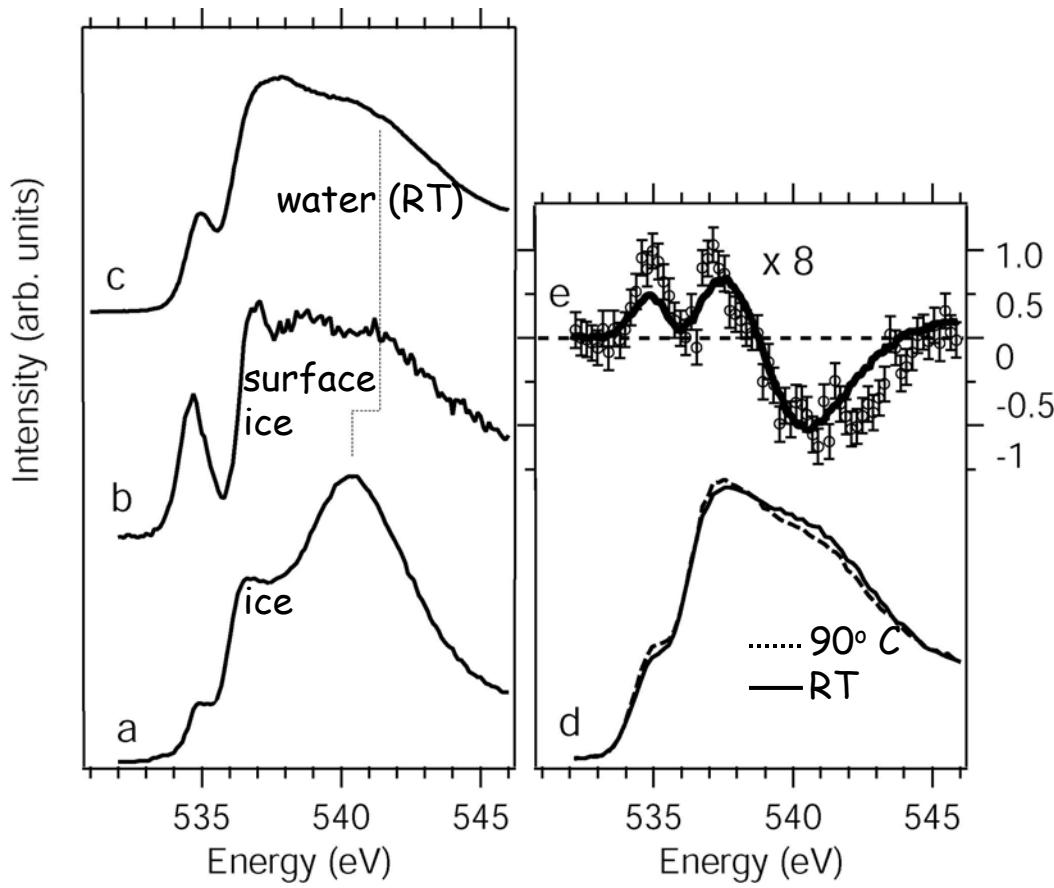
### in particular:

- systems not suited for studies with conventional techniques
- concentrated low  $Z$  systems
- liquids
- reactive specimens

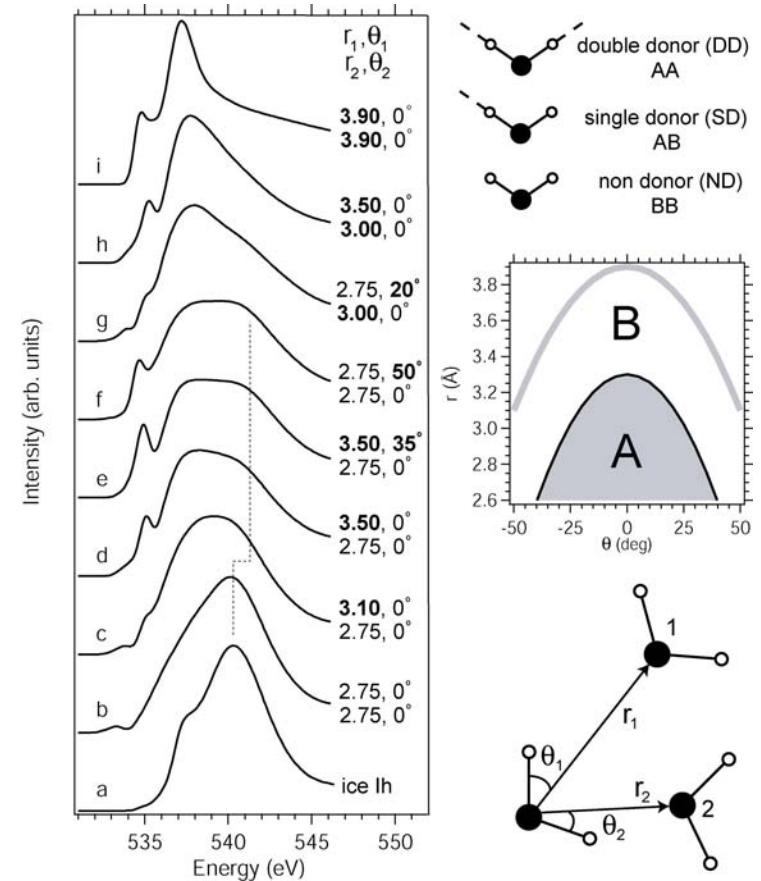
# Local Structure of Water



data



calculations



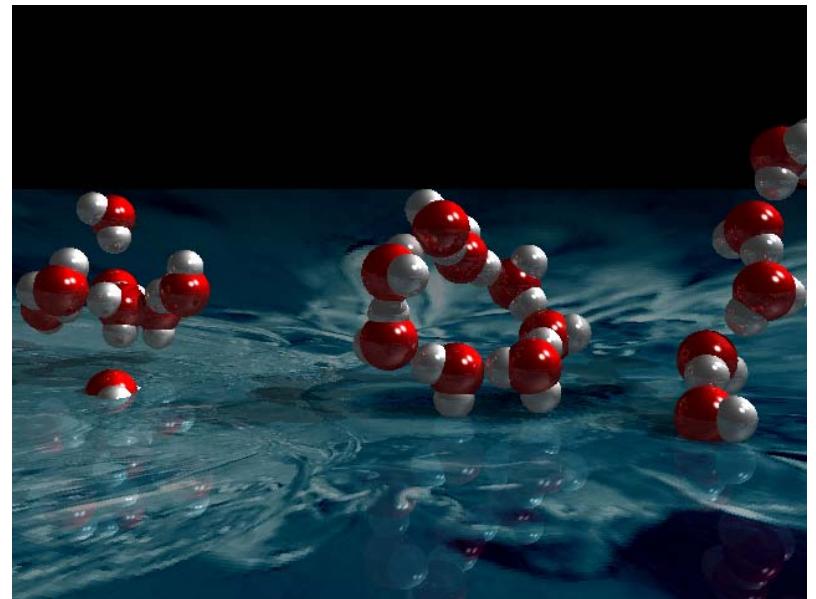
# What the data suggest

- identification of large percentage of molecules with one 'broken' donor bond (SD)  
⇒ indication of ring like configurations
- weak temperature dependence

## hydrogen bonds per molecule

Temperature	25°C	90°C
MD	~3.5	~3.3
experiment	~2.1	~2

Wernet et al, Science accepted

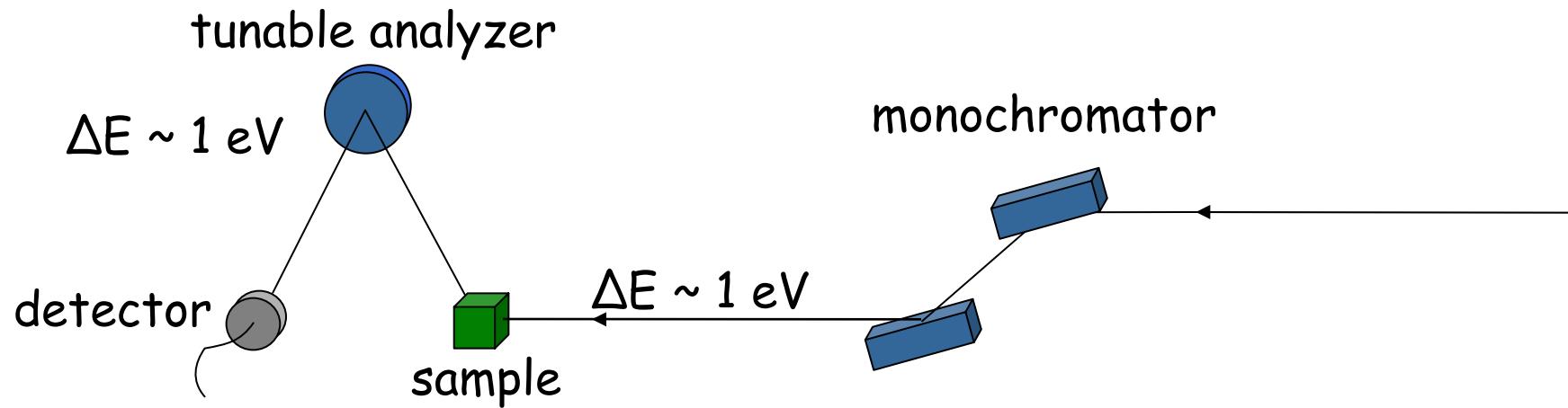


classical MD uses pair potentials

⇒ possibly incomplete description of hydrogen bonds

needed: *ab initio* MD simulations with > 500 molecules

# Photon-in Photon-out X-ray Spectroscopy



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# Motivation

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## why XES?

- direct probe of unpaired spins in 3d transition metals  
    ⇒ oxidation state, spin state
- sensitivity to ligand type and distance
- 'orientation' of disordered sample

future: pump probe, single shot experiments (LCLS)

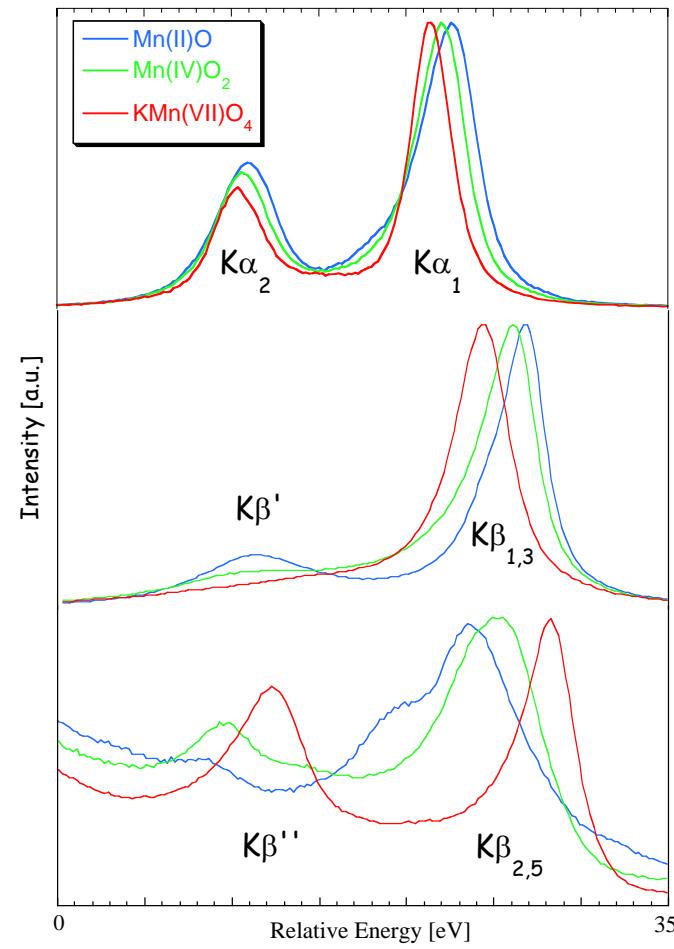
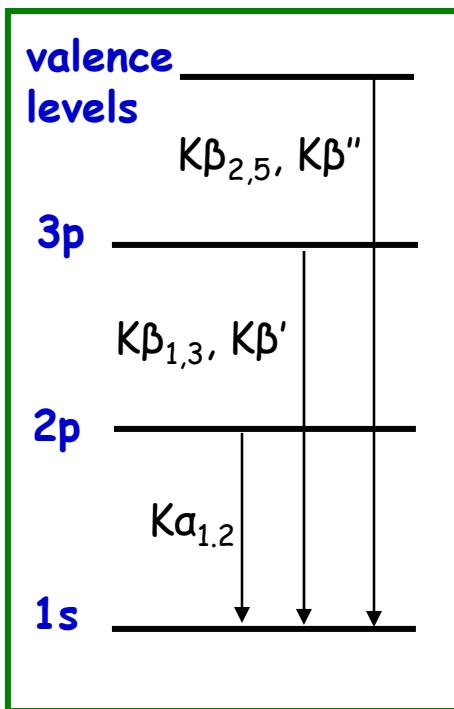
## samples (5-12 keV)

- any sample (very dilute sample possible)
- 3d transition metals (K-emission)
- rare earths (L-emission)

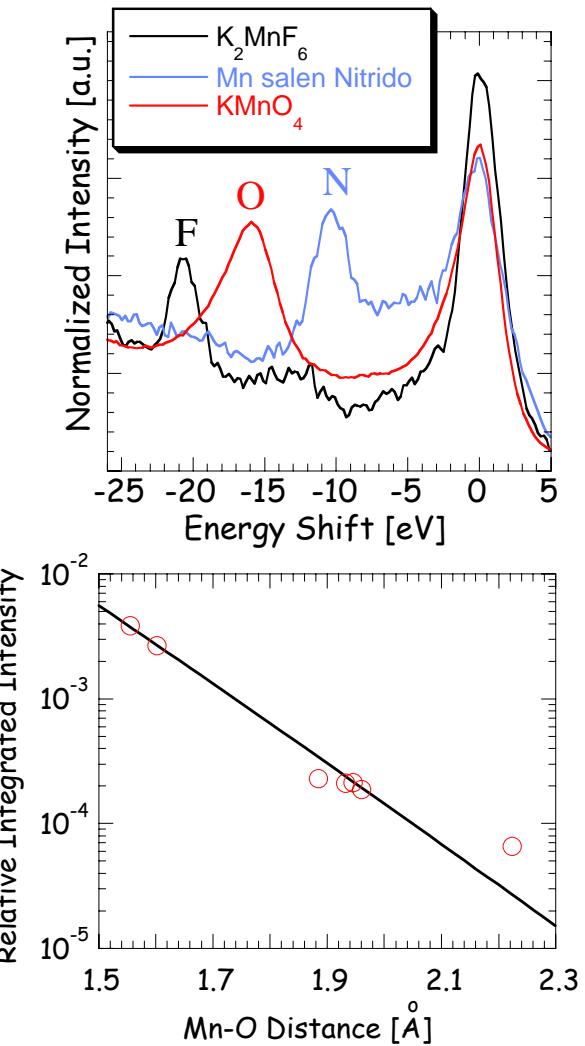
# X-ray Emission Spectroscopy

## chemical sensitivity of K fluorescence

level diagram



Bergmann et al, Chem Phys Lett 302, 1999

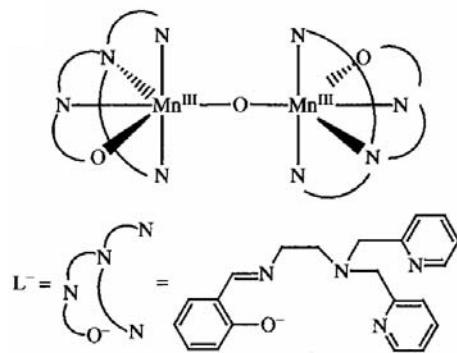


# Comparison: XANES versus K $\beta_{1,3}$ XES

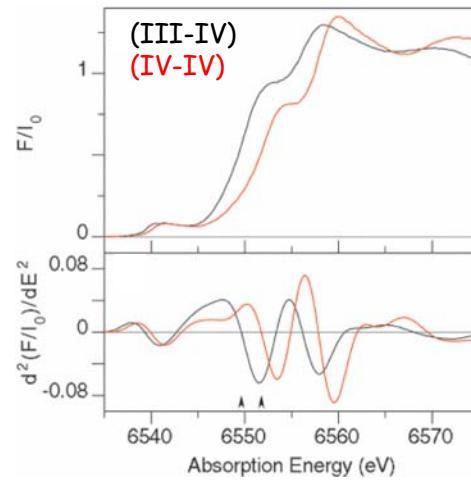
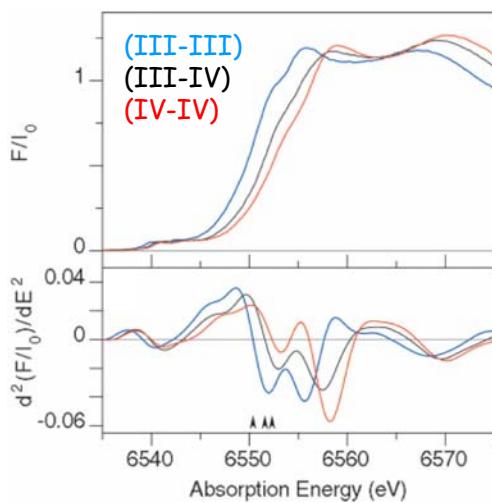
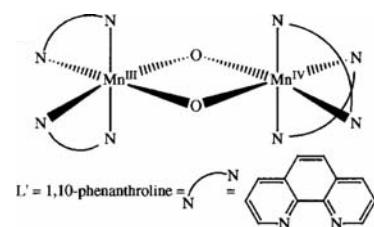


## XANES spectra

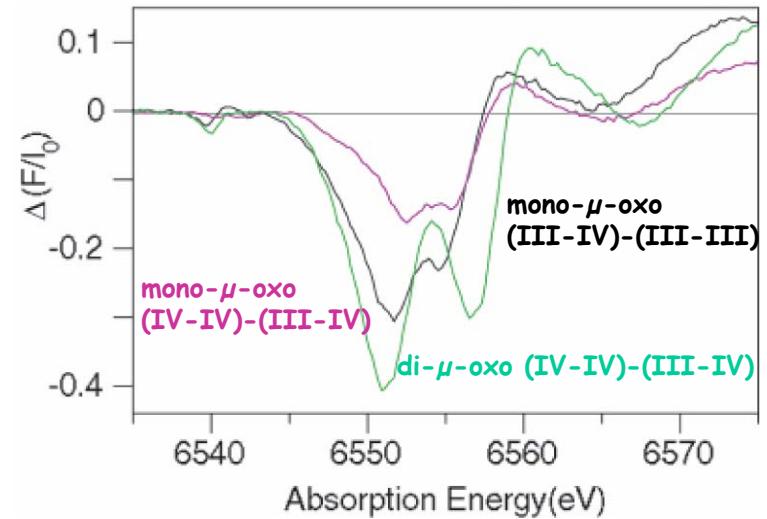
**mono- $\mu$ -oxo  
manganese**



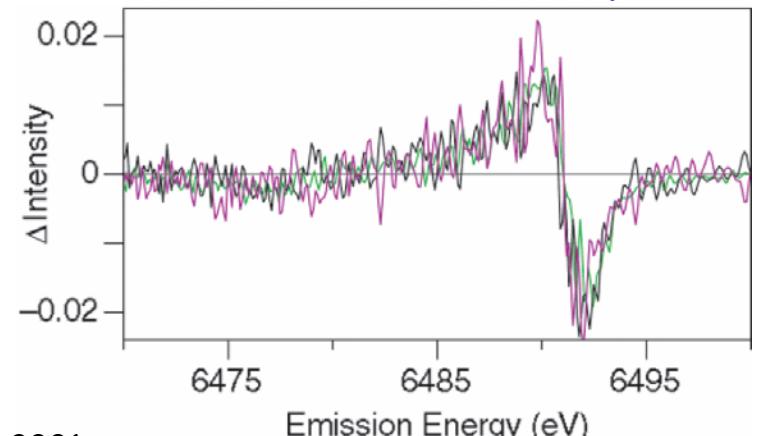
**di- $\mu$ -oxo  
manganese**



## XANES difference spectra

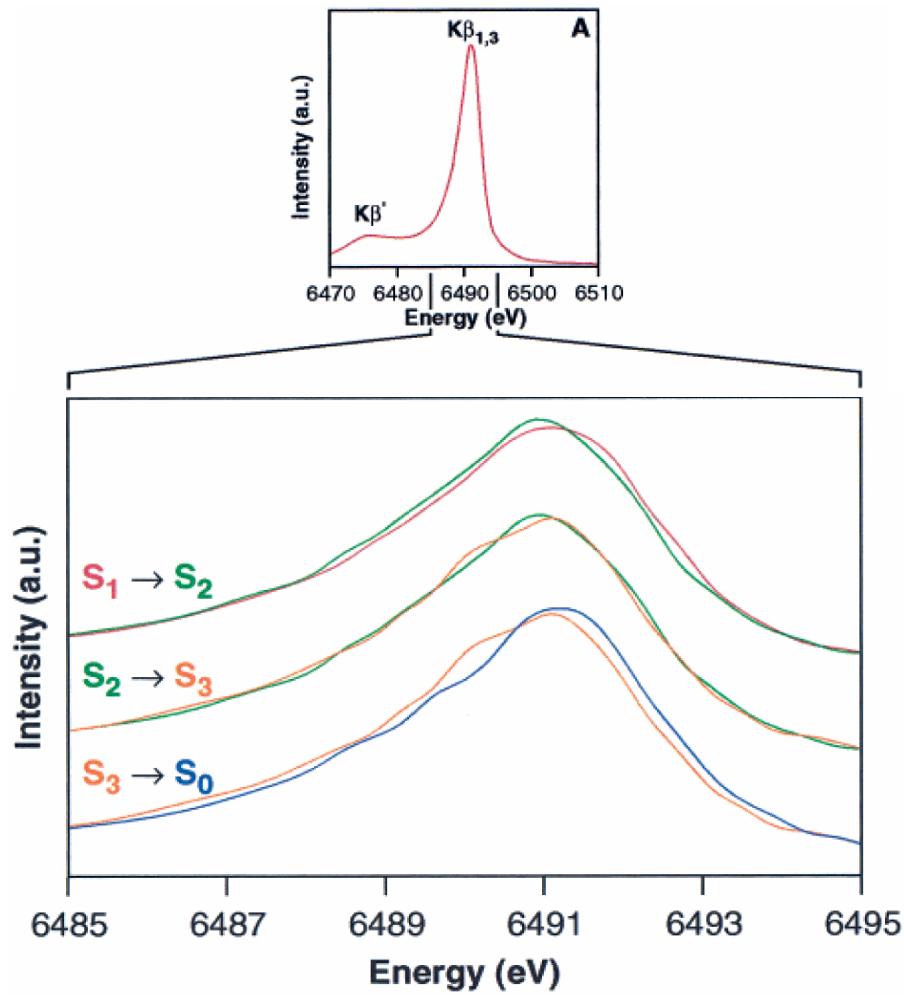


## K $\beta$ XES difference spectra

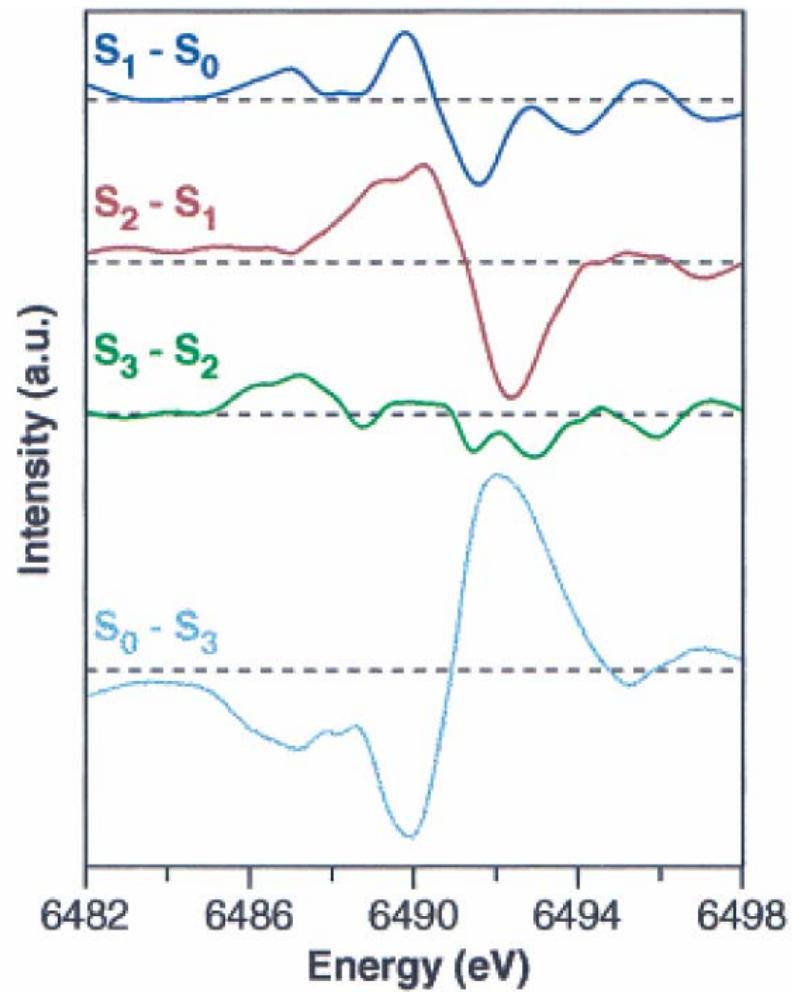


Visser et al, JACS 123 7031, 2001

# $K\beta_{1,3}$ XES on Photosystem II

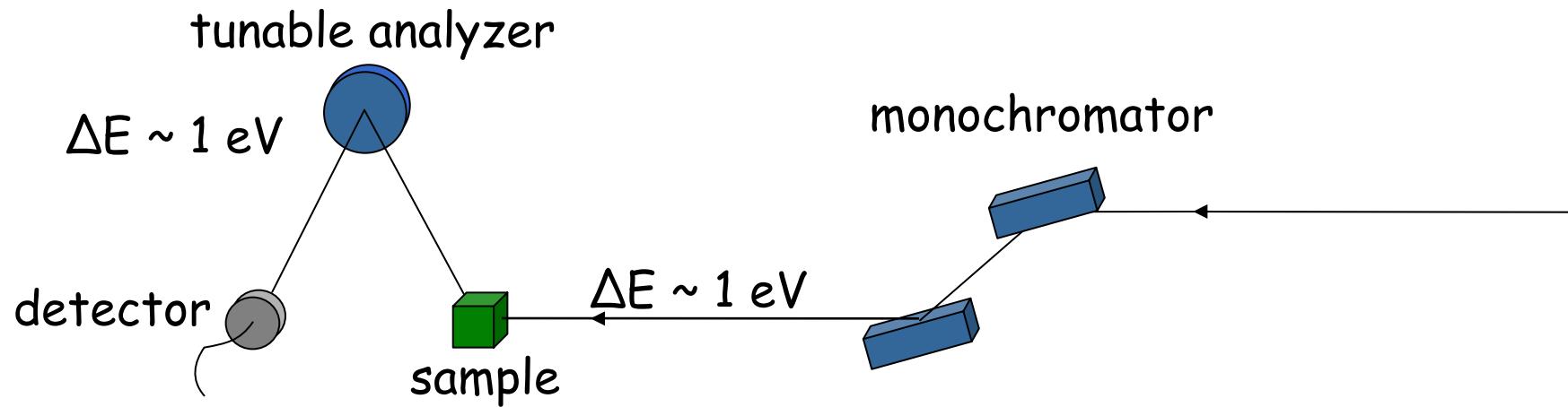


difference spectra



Messinger et al, JACS 123, 7804, 2001

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# Motivation

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## why selective selective EXAFS?

- chemical in addition to elemental specificity
- extended k-range  $\Rightarrow$  higher resolution

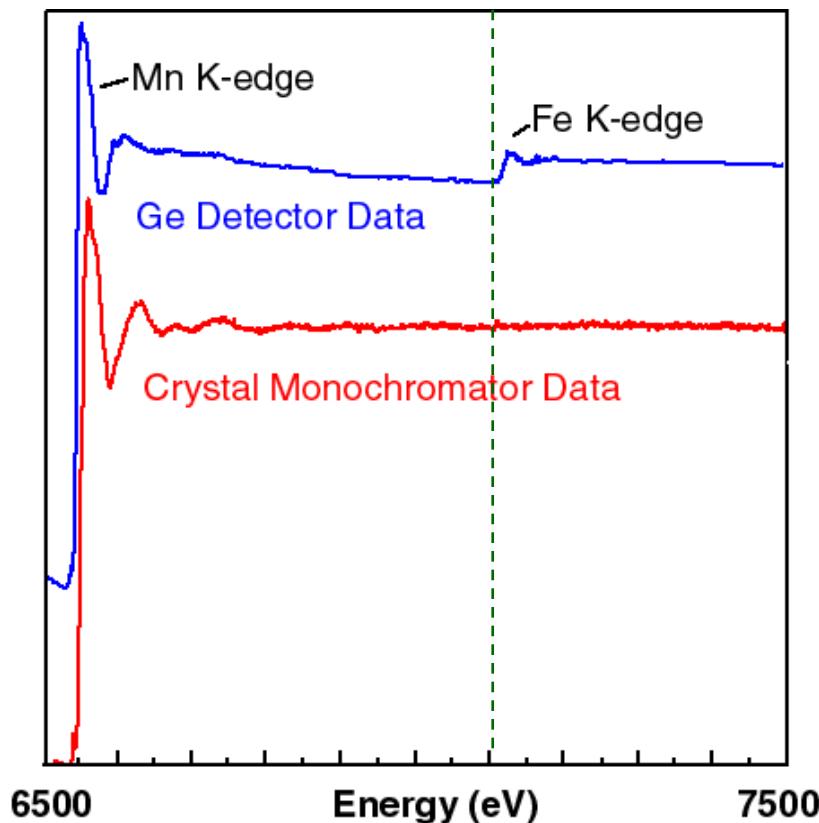
## samples

- any sample
- e.g. 3d metals, rare earths

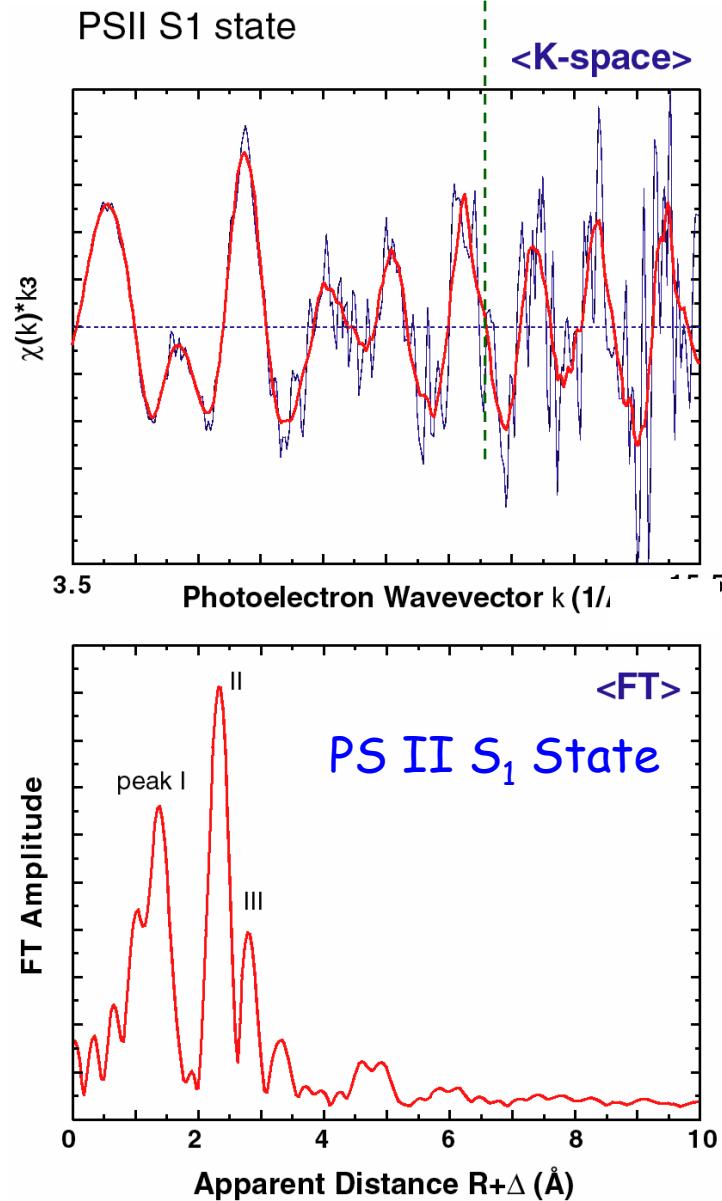
# Selective X-ray Absorption Spectroscopy



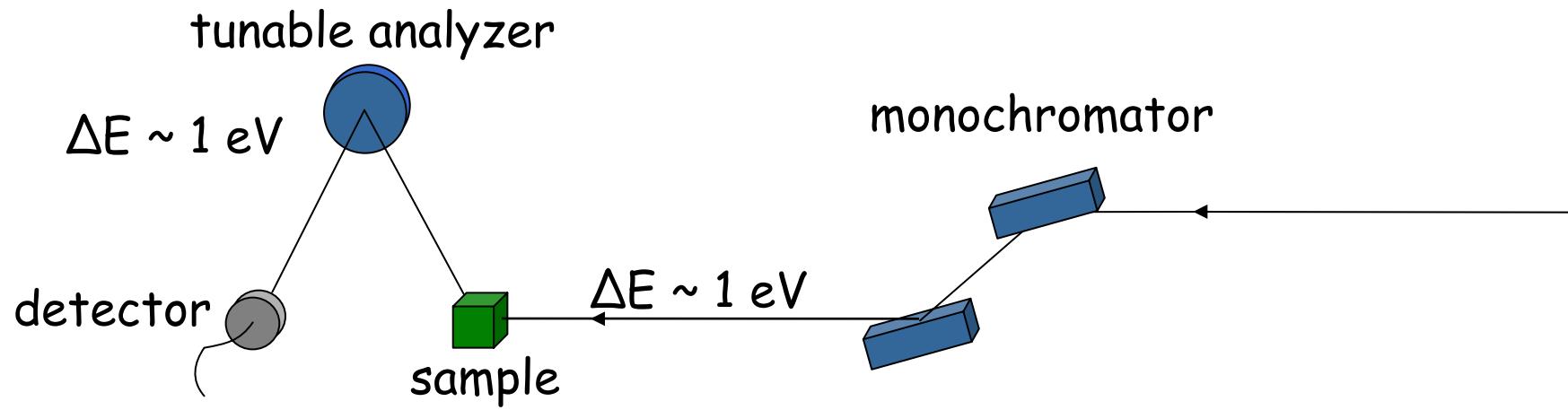
Extending the Resolution of EXAFS from 0.15 to 0.10 Å



$S_1$  : 2 to 3 Mn-Mn at 2.72 - 2.84 Å  
 $S_2$  : 2 to 3 Mn-Mn at 2.71 - 2.77 Å



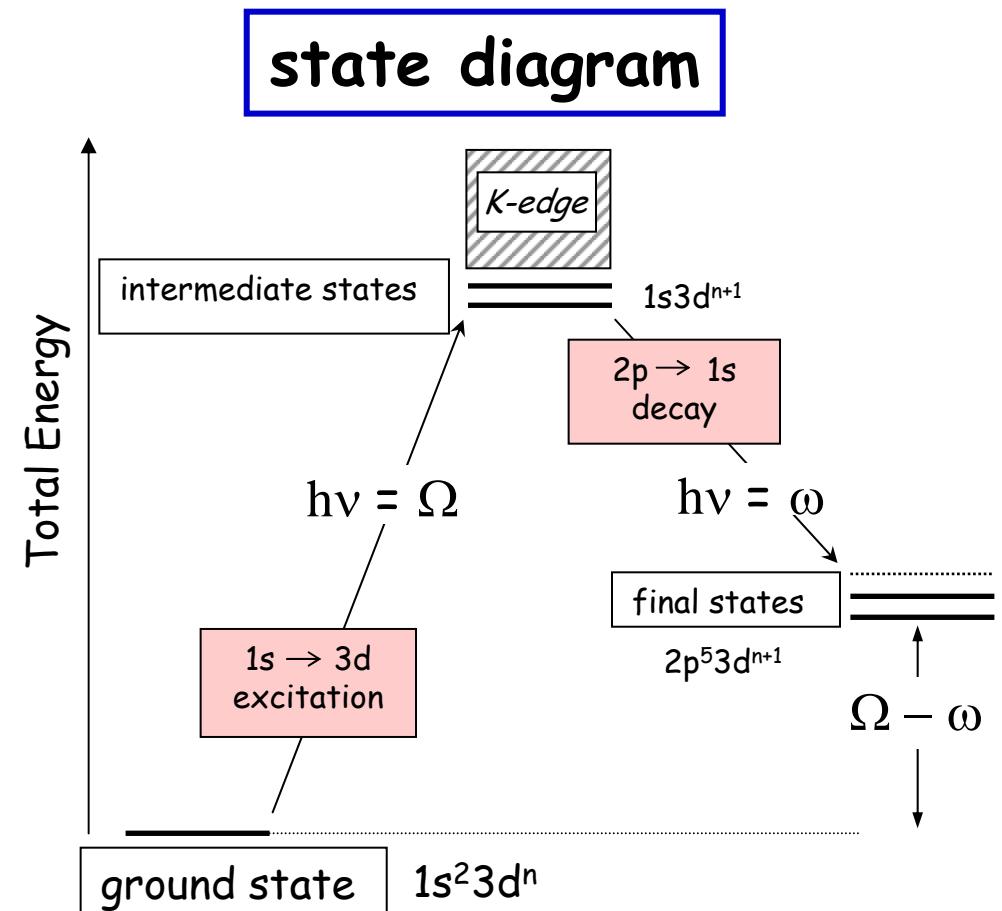
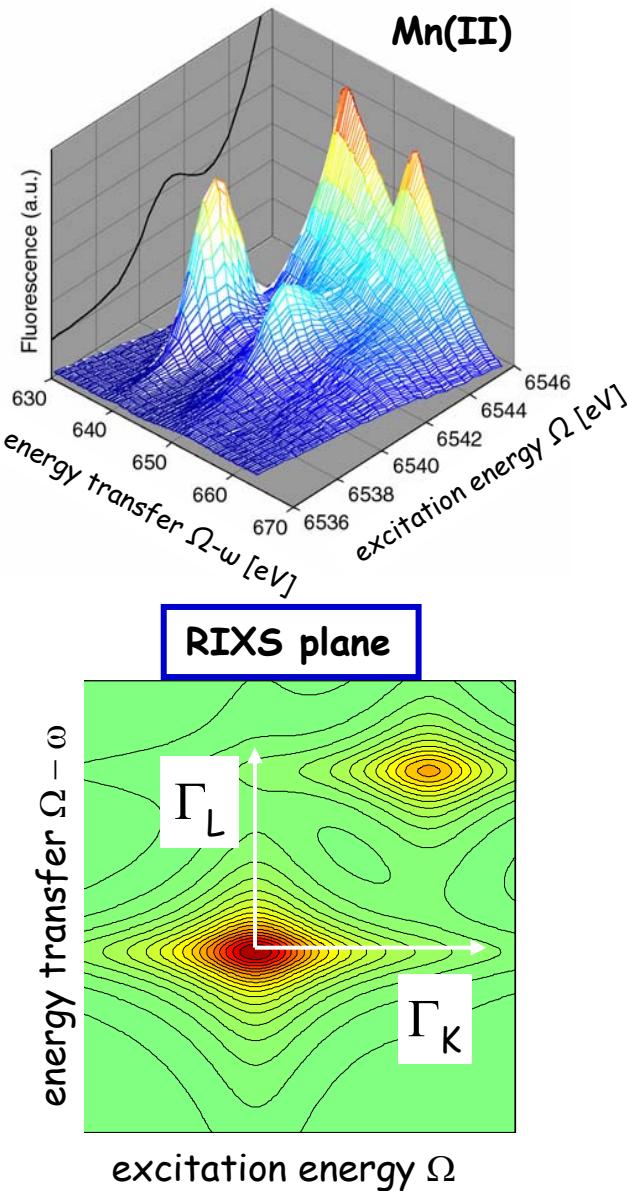
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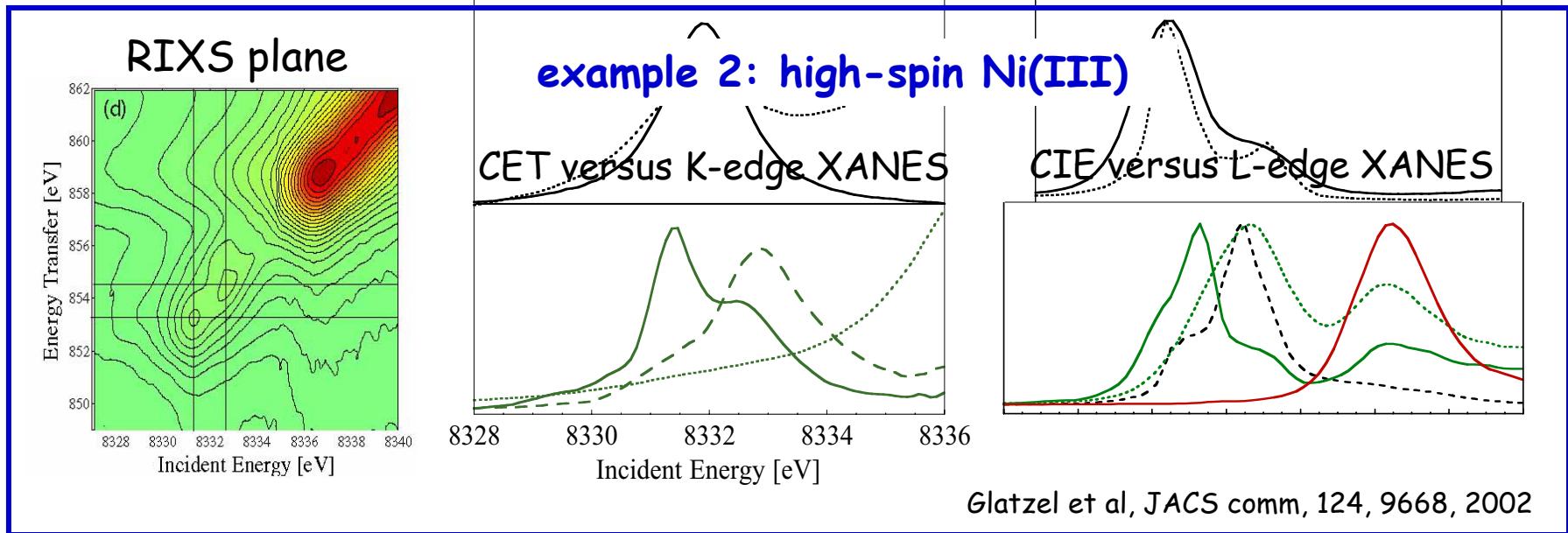
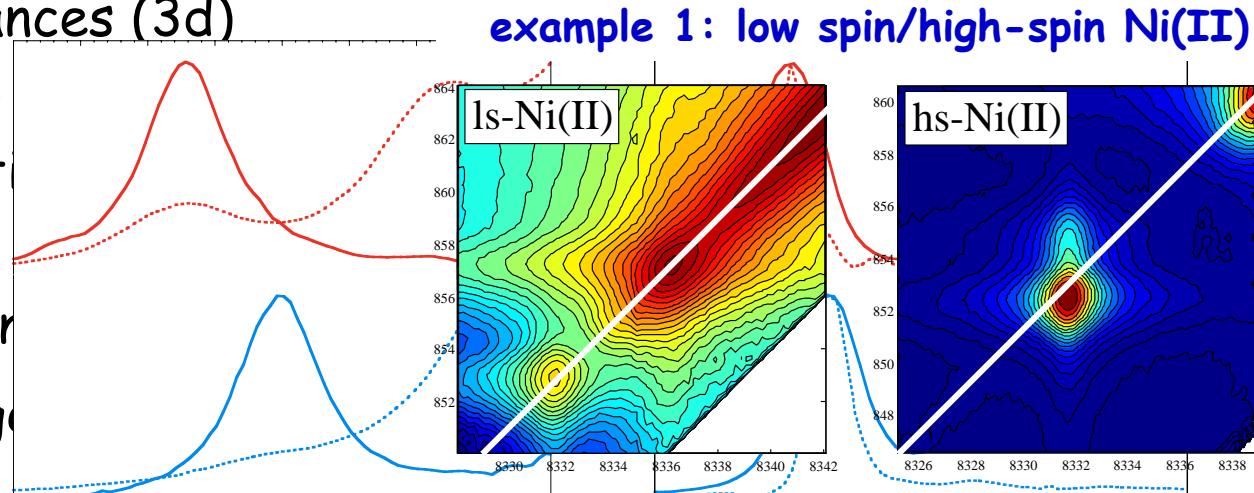
# Principle of RIXS (1s, 2p)



# Why RIXS?



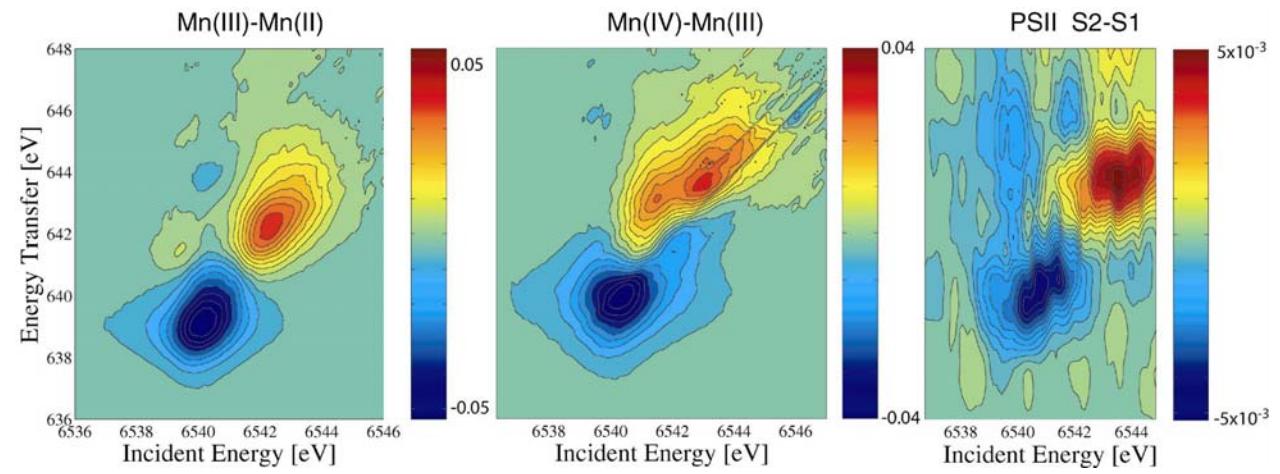
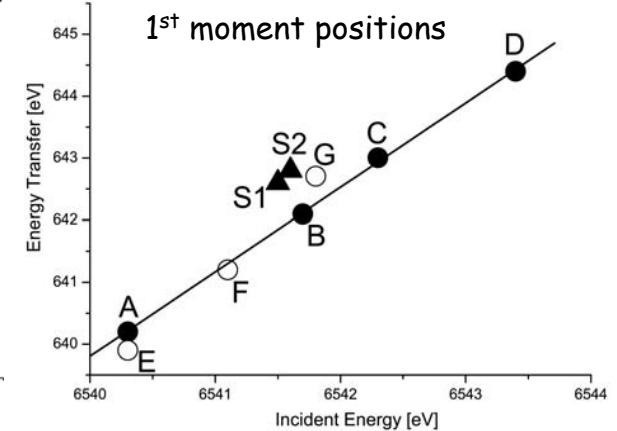
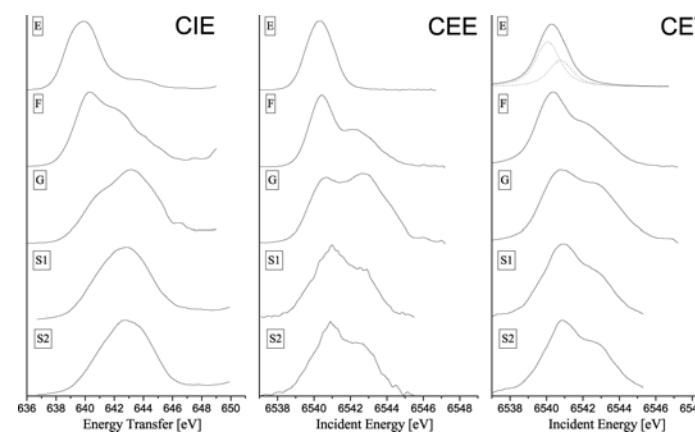
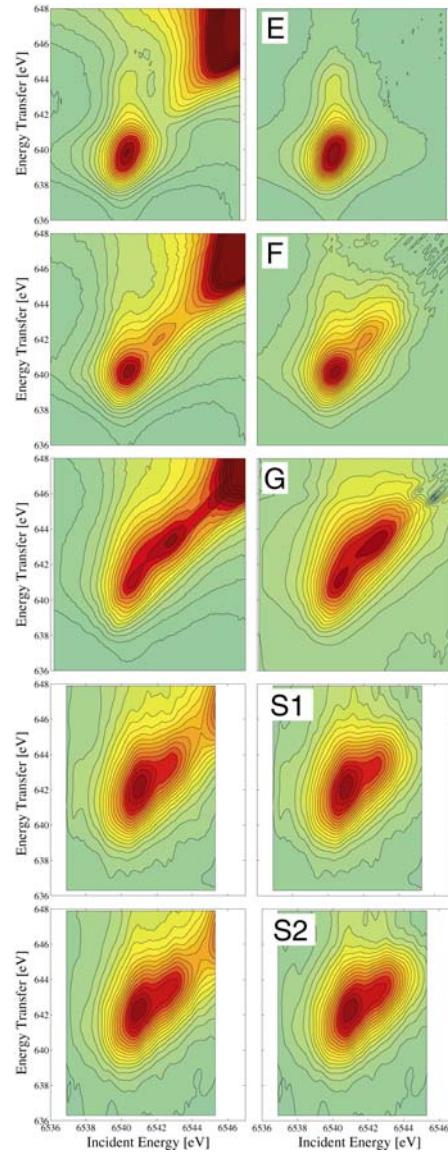
- isolate LUMO resonances (3d)  
→ orbital population,
- L-edge like information  
→ sensitivity to spin
- less lifetime broadening
- less radiation damage



# RIXS Spectra of Mn models and PSII



E:  $\text{MnII}(\text{acac})_2(\text{H}_2\text{O})_2$  F:  $\text{MnIII}(\text{acac})_3$  G:  $\text{MnIV}(\text{sal})_2(\text{bipy})$



Glatzel et al, JACS, submitted



# Conclusions

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- XRS: low Z systems, non dipole DOS, EXAFS possible
- XES: spin state, chemical state, neighbor distance and type
- S-XAS: extended k-range, chemical/spin specificity
- RIXS: isolate LUMO resonances  
L-edge/M-edge like information with hard x-rays

## Future

- better resolution, more efficient spectrometers
- lots of photons

planned 'Advanced Spectroscopy and Inelastic Scattering Facility'  
at SPEAR3, first workshop see:

[http://www-srsl.slac.stanford.edu/conferences/ssrl30/IXS\\_report.pdf](http://www-srsl.slac.stanford.edu/conferences/ssrl30/IXS_report.pdf)



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# End of Show

# Comparison of Mn(II), Mn(III) and Mn(IV) 1s,2p RIXS

